SEDIMENTATION EQUILIBRIA OF COLLOIDAL PARTICLES*

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Abstract

The purpose of this work was to find the distribution law of colloidal particles for sedimentation equilibrium in large cells, in which uniform concentrations had been observed by Burton, Porter and Laird. We took great care to eliminate effects which might prevent an equilibrium state. Gold particles prepared by the Zsigmondy nuclear method were allowed to settle several days in a quartz cell in a carefully controlled thermostat bath. The steady state was determined by taking visual ultra-microscopic counts on different days. The La Place-Perrin exponential law of distribution was found to hold as demanded by the kinetic theory.

Introduction

UNTIL recent years it seemed quite well established that colloidal particles obey in their Brownian movement and related phenomena the simple laws of the kinetic theory when no forces operate between the particles. Thus, in the early work on sedimentation equilibria with colloids in a gravitational field, Perrin[1] and Westgren[2] found results in agreement with the familiar La Place-Einstein distribution law, which the molecules of the atmosphere obey; namely:

$$\log n = \log n_0 - Nvgh(\rho_1 - \rho_2)/RT.$$

In this equation n is the concentration of particles at the height h above a given point of reference, n_0 is the concentration of particles at the reference point, v is the volume of a particle, ρ_1 is the density of the particles, ρ_2 is the density of the medium in which the particles are dispersed, g is the gravitational acceleration constant, R is the gas constant and T is the absolute temperature. Each of the two above-mentioned men used cells constructed of microscope slides and cover glasses, the depth of the cells used by Perrin being in general about 0.1 mm. The very careful work of Westgren, who observed through ranges as great as 1.1 mm in thin cells of presumably much greater depth than the range of observation, yielded a value of N which checks very closely the accepted value.

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** American Petroleum Institute Research Fellows.

[1] Perrin, "Brownian Movement and Molecular Reality," page 41.

[2] Westgren, Zeits. f. Phys. Chemie 89, 63 (1915).

However, later workers in the field of colloids noticed that the particles in larger containers often remained in suspension over long periods of time without any apparent sedimentation. This seemed to be in contradiction with the La Place-Einstein law and investigations on distributions in sols five millimeters or more in depth were carried out by Burton,[3] Porter[4] and Laird,[5] who reported a uniform distribution throughout the greater portion of the sol. In attempts to explain such a distribution, Burton suggested the existence of electrical forces acting between the particles while Porter assumed that his sol was so concentrated that the osmotic pressure of the colloidal solution no longer followed the simple law of dilute solutions; in other words, he introduced a volume term which acts like the b in van der Waal's equation. Although Porter introduced the b term arbitrarily, he suggested that if it should have a physical significance, in order to get the requisite size he must assume a concentration of the liquid upon the particles of the suspension. Others have suggested that the apparent contradiction might be due to insufficient precautions in the eliminating of convection or insufficient time in waiting for the attainment of the equilibrium of colloids in deep cells. Kraemer[6] has made a very illuminating discussion of the whole field, so that it is hardly necessary to present a great amount of critical detail.

At this point, it might be well to mention that Rinde[7] has determined the equilibrium distribution of gold colloids in a high centrifugal field produced by an ultra-centrifuge. The range shown in his plot extends over a distance of more than three millimeters and although the exponential law seems to hold in a layer about 0.5 mm thick, there is a slight deviation from this law in the remainder of the distance.

Since some knowledge of the electrical nature of colloids had already been gained from the study of electrocapillary phenomena, the possibility of forces acting between colloidal particles in such a manner as to become manifest in sedimentation equilibria was of great interest. In fact, the possibility of any factor which would upset the La Place-Einstein law seemed very important for the understanding of all phenomena in which finely divided matter is in contact with liquid. Thus, it seemed worth while for us to attack the problem of sedimentation equilibria in deep cells taking great care to eliminate spurious effects, which might account for a uniform distribution, in particular to avoid convection currents in the sol, to prepare colloids with little variation in size, and to wait a sufficient time for equilibrium to be attained.

Experimental Work

In our work, we used gold sols enclosed in a cell 8.3 mm in height. This cell was constructed of quartz which is much more insoluble in water than glass.

[3] Burton and Bishop, Proc. Roy. Soc. **A100,** 414 (1922); Burton and Currie, Phil. Mag. **47,** 721 (1924).

[4] Porter and Hedges, Phil. Mag. **44,** 641 (1922).

[5] Laird, Jour. Phys. Chem. **31,** 1034 (1927).

[6] Kraemer, "Colloid Symposium Monograph," Vol. V, p. 81.

[7] Rinde, Diss. Upsala, p. 200 (1928).

It is important not to pollute the sol since gold sols are quite sensitive to electrolytes as regards stability. The colloidal solution was allowed to settle undisturbed for several days inside a thermostat system which was capable of holding the temperature constant to within a few thousandths of a degree Centigrade. It was necessary that temperature gradients, which cause disturbing convection currents in the cell, be avoided. The distribution curve was then found by taking visual ultra-microscopic counts at successive levels within the cell's height. The thermostat control was so little affected by the heat from the arc and the observer during the period of observation that there was a temperature rise of only a few thousandths of a degree Centigrade. Thus, the distribution could be determined and compared on different days.

A cross section of the cylindrical quartz cell is shown in Figure 1.

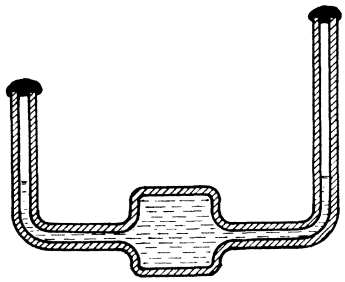

Fig. 1. Cross section of cylindrical quartz cell.

The vertical wall was made of tubing about 8 or 9 mm in inside diameter, the ends of which were ground in order that flat plates could be fused on to form the top and bottom of the cell. The two small L-shaped tubes were sealed into opposite sides of the tubing in order to make possible cleaning and filling of the cell. After the filling with colloidal solution, these side tubes were closed with sealing wax as shown in the diagram.

A great amount of effort was spent on the phase of the problem having to do with temperature control. In the final system, the cell was clamped inside a trough well insulated thermally inside the wooden case marked *C* in the photograph in Figure 2. The cell was immersed in a stream of water, pumped through the trough from a large thermostat tank whose dimensions were $16'' \times 18'' \times 27''$. The connections between the trough and the tank were made inside the insulating material shown in the lower left hand corner of the photograph. The temperature of the water in the trough was obtained by means of the Beckmann thermometer *B*. A view of the assembled apparatus is shown from the opposite side in the photograph in Figure 3, in which the tank is marked *T*. The water was kept in turbulent motion in the tank by means of a large stirring propellor which was rotated by the motor as seen in the photograph. Immersed in this tank was a thermostat regulator made of glass tubing filled with carbon tetrachloride, which has a high thermal coefficient of expansion. This regulator operated a relay to the heating element by means of a vacuum tube circuit mounted on the top of the tank near-by the

relay. With this circuit practically no current flowed through the mercury contact in the regulator.

In Figure 3 a part of the optical system can be seen mounted on the sturdy wooden frame to the left of the tank. The entire optical system was built on the heavy metal carriage *L*. The colloidal solution was illuminated by means of the carbon arc *A*, the light from which was passed through the copper chloride absorption cell *H* in order that the beam which was transmitted should have little heating effect. Next the beam was passed through a paraboloidal condensing lens, a16 mm microscope objective and a glass window in the trough immediately in front of the cell. The beam was transmitted into the cell through the curved wall and was brought to a focus in a fairly small pencil inside the cell. Observations were made with the microscope *M* in Figure 2, suspended on the carriage directly above the cell. This microscope consisted of the vertical tube made of Bakelite for thermal insulation, an objective with a focal length of 16 mm immersed in the water of the trough, and a hyperplane eyepiece containing a scale divided into squares, one of

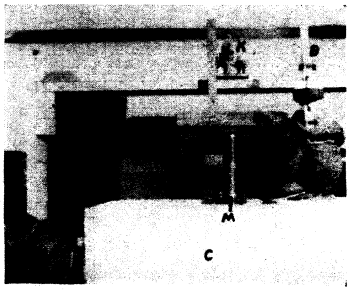

Fig. 2.

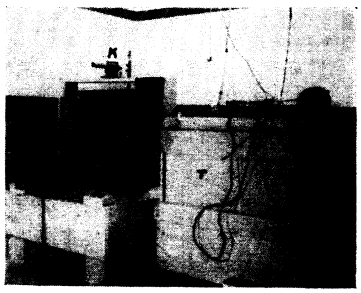

Fig. 3.

which was divided into smaller squares. The focal plane of the microscope fell within the pencil of light inside the cell and counts of the numbers of colloids inside squares could be made. Various levels in the cell could be observed by raising or lowering the entire carriage by means of four screws upon which were mounted divided heads. Two of these screws *S* can be seen in Figure 3. Large changes in height could be read from the screw-heads while small changes could be read by means of the cathetometer *K*.

Gold sols were prepared by the Zsigmondy nuclear method,[8] which was used by Westgren and is perhaps the most highly recommended for obtaining particles closely uniform in size. The La Place-Einstein law is, of course, valid only for particles having a definite radius and a definite mass. The nuclear sol was formed by the reduction of gold chloride by phosphorus dissolved in ethyl alcohol. The nuclei were enlarged in two steps by the reduction of gold chloride upon the particles by means of hydrogen peroxide (30 percent). The sol upon which observations were made was obtained by diluting this gold sol. In this preparation, it was highly important to obtain water low in both sus-

[8] Rinde, Diss. Upsala, p. 25 (1928).

pended matter and electrolyte content. A special still was constructed which employed the partial condensation of steam from water treated with potassium permanganate and potassium carbonate. The steam was passed through a settling chamber and a tin condensation tube. The water was collected in a Jena glass bottle.

Results

We shall show distribution curves for two different sols which contained particles approximately the same size, but were different in initial concentration. The temperature control for the more dilute sol was not as good all of the time as might have been desired. Also, one or two small bubbles were observed in the top of the cell when it was removed. However, the consistency of

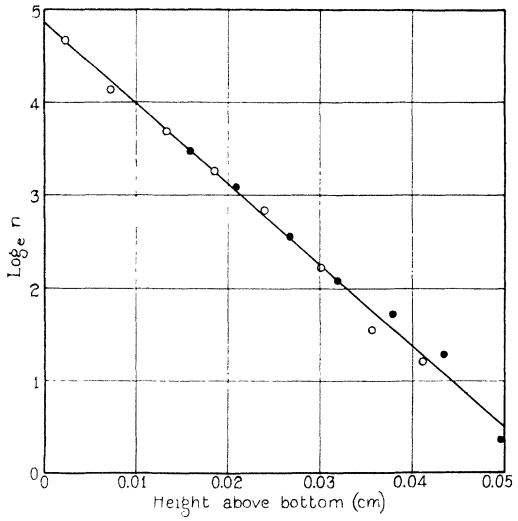

Fig. 4.

the results would indicate that no serious disturbances were set up, as one may see in Figure 4 where logarithms of concentration values are plotted as ordinates, and in Figure 5 where the same concentration values are plotted in the ordinate direction. Each of the points shown is taken from 50 counts with the exception of the two lowest points marked with circles which are taken from 25 counts. The points marked with dots were taken after about 3 days of sedimentation while the points marked with circles were taken from the same sol after about 5 days. The concentration at the end of 5 days in the upper regions was roughly one-half percent of the highest concentration observed. Such a value is even lower than the lowest point shown, so that the distribution curve lies very close to the zero axis in the upper part of the cell. This portion of the curve was somewhat higher as observed at the end of three days of sedimentation, the concentration near the top being almost as great as that shown by the lowest point plotted and also being greater than the concentration in an intermediate region. This latter would indicate that there might

have been a slight disturbance in the upper regions which was of practically no consequence in the immediate neighborhood of the bottom, where, after all, the bulk of the particles in which one is interested was located. The impor-

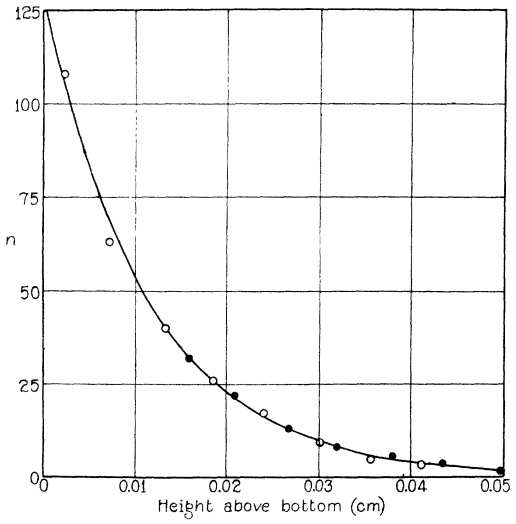

Fig. 5.

tant fact is that a steady state was reached and the distribution of the particles in this state was exponential. The slope of the curve shown in Figure 4 is 87; the temperature was 26.5°C.

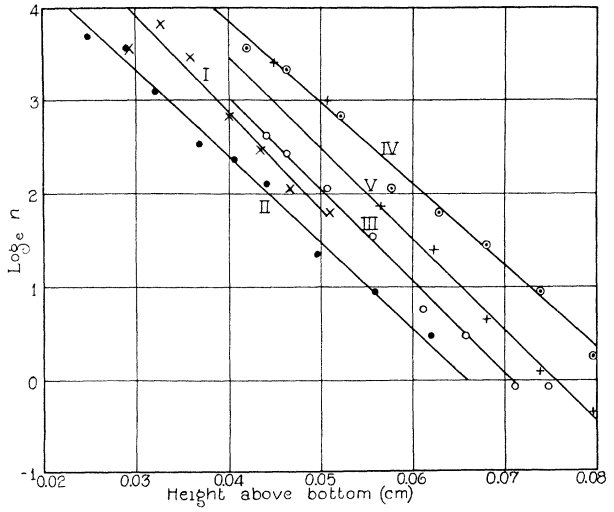

Fig. 6.

The second sol which was of higher concentration was unusually stable and the cell was allowed to remain in the thermostat for a period of about two

weeks. During the first three days of sedimentation, the two extreme temperatures observed differed by only 0.005°C, so that for long periods of time, the temperature was scarcely seen to vary on the Beckmann thermometer. The temperature was maintained at 26.5°C. Curves I to V shown in Figure 6 were obtained after sedimentation periods of 3, 5, 8, 9, and 10 days respectively. At each level marked by a point, a total of 50 counts was taken. It should be mentioned that the counts were made with quite a little difficulty due to the scattering of light near the bottom of the cell (in a large measure from the dense layer of colloids), the shifting of the light pencil due to changes of the arc, and the psychological factor attendant with such counts. However, the slopes of the curves are fairly consistent and the average is 96. The relative displacements of the curves were perhaps in a large measure due to the experimental error in locating the bottom with respect to the points, although it is not certain that actual shifts of the distribution did not occur. Certainly, it is more difficult to avoid slight disturbances in the regions observed in Figure 6 than those in Figure 4 since these regions are further removed from the damping surface at the bottom. In any case, whether the displacements were real or not, the effect was certainly of no prime importance as regards the distribution law which is seen to be exponential in character. In this solution the colloidal particles became remarkably scarce in the upper regions. On the ninth day, the concentrations observed in the main body of the sol were of the same order as those observed on the fifth day for the other sol, and thus were relatively slight since the latter sol was much the less concentrated of the two initially. This scarcity of particles is important since the distribution curve should approach the zero axis very rapidly upwards. The slight upward displacement of the experimental curve above the theoretical curve in the upper regions might be due to the lateral diffusion of particles into the cell from the side arms, the presence of particles differing in size or density from the bulk of the gold particles, and perhaps the presence of undetected slight movements of the sol.

Discussion

As has been pointed out by others, it is likely that both Burton and Porter did not take sufficient precautions against disturbing convection currents. Burton and Bishop,[9] working with copper colloids, used a large tube 94 cm long without much care in this respect. Burton and Currie,[10] working with gamboge, arsenious sulphide, Bredig copper and Bredig silver colloids, repeated the work using 145 cm tubes immersed almost completely in a thermally insulated bath. They state that this bath was stirred "from time to time" and that the temperature of the room varied slowly over a range of 7°C during the period of four months of sedimentation. It is very doubtful if such conditions were satisfactory. Porter and Hedges[11] working with gamboge particles, fractionally centrifuged to obtain uniformity in size, reported that

[9] Reference 3.
[10] Reference 3.
[11] Reference 4.

although the distribution was uniform in the greater portion of their cell's height, the concentration diminished near the top as the top was approached. We, also, found a similar distribution in our early work when there were disturbing currents. In addition, however, we found an increase in concentration near the bottom. It is unfortunate that Porter did not investigate the region in the immediate neighborhood of the bottom, although it is quite surprising he found no appreciable increase in concentration in the lowest level he reached. Barkas[12] working under Porter stated that convection currents were quite a disturbing factor in his work. It is very easily seen how there could be a settling of particles in the neighborhood of a surface even though convection currents were stirring up the particles in the central portion of the sol since the frictional drag at the surface would prevent appreciable currents from being set in motion in that neighborhood. Thus one might expect to find the diminishing concentration near the top.

Then there is the phase of the problem which concerns the time necessary for sedimentation equilibrium to be attained. The theoretical work on sedimentation has been done by Mason and Weaver[13] and Fürth.[14] Weaver[15] laid down the general rule that equilibrium should be attained within the time that it takes a particle to settle twice the depth of the cell according to Stokes' law. Later Fürth[16] stated more rigorously that the necessary time is proportional to the cell depth when RT/NXl is large, and proportional to the square of the cell depth when this quantity is small. In this expression, which is called α by Mason and Weaver, X is the resultant gravitational force acting on the particle and l is the cell depth. Fürth estimated that it would take a number of years for equilibrium to be attained in Burton's work. As already stated, the time of sedimentation was only four months. It must be mentioned that the whole problem in Burton's case is very indefinite since he did not use particles of uniform size. As pointed out by others, since Porter does not state the length of time allowed for sedimentation, it is quite possible that he did not wait long enough for equilibrium conditions. Fürth pointed out the similarity between Porter's curve and the theoretical transient state curve. In our work, we have calculated the time necessary for a gold particle to settle twice the height of the cell for the sol of Figure 4, taking the slope of the equilibrium curve to be 87. The value of the radius obtained from the La Place-Einstein equation is 3.6×10^{-6} cm. From Stokes' law, the time of settling a distance of twice our cell depth, or 1.66 cm is 76 hours or about three days. A steady state was apparently reached in our work in about 3 to 5 days. Thus, it seems that the Weaver rule holds roughly in our case. Our value of α is 0.014.

Burton[17] explained the uniform distribution curve by assuming that the colloidal particles are electrically charged and repel each other. Porter

[12] Barkas, Trans. Far. Soc. **21**, 66 (1925).
[13] Mason and Weaver, Phys. Rev. **23**, 412 (1924).
[14] Fürth, Zeits. f. Phys. **40**, 351 (1927).
[15] Weaver, Phys. Rev. **27**, 499 (1926).
[16] Fürth, Zeits. f. Physik **45**, 83 (1927).
[17] Burton, "The Physical Properties of Colloidal Solutions," p. 87.

criticised this theory by stating that the particles would tend to move to the walls of the containing vessel in such a case.

Burton[18] also suggested that the settling of colloids may be prevented by Bownian movement and defined as the "critical radius," that radius for which the particle is displaced by Brownian movement in one second the same distance through which it would fall in one second according to Stokes' law. Particles with radii smaller than this so-called critical radius would remain in suspension without sedimentation. Now, of course, as Kraemer has pointed out, Brownian movement takes place in no favored direction and it is obvious from our results that settling did take place. The critical radius of gold is several times our radius since Burton gives 28×10^{-6} cm as the critical radius of platinum, which is heavier than gold.

Porter has suggested that his results were due to the fact that his sol was no longer dilute. His concentration of gamboge particles was of the order of 10^7 per cc. From our work, the concentration represented by the highest point plotted in Figure 5 is of the order of 4×10^8 per cc. Porter's value of concentration seems far too low to justify his assumption of a concentrated sol, especially in comparison with the concentrations used by the earlier workers.

Porter has also suggested that there are three distinctive regions in a colloidal solution: the Gibbs layer located very close to the surface, the "Perrin layer" in which the colloids are distributed exponentally in a layer a fraction of a mm in thickness near the top of the vessel, and finally "a layer of one or two millimeters' thickness (in the particular cases studied in this paper), in which a further change of concentration occurs which can not be calculated in the way adopted by Perrin." The third region is close above the principal part of the sol in which the concentration is constant. From our results, we have concluded that in the case of particles more dense than water in deep cells the particles are distributed in a "Perrin layer" extending from the bottom upwards. Whether this layer extends appreciably up through the main body of the sol should depend upon the height of the vessel, the radius and the density of the particles, and the initial concentration of the particles. Certainly if one should look for an anomaly in the distribution law due to high concentration, the logical region to investigate is that near the bottom of the cell where high concentrations may be obtained. In fact Constantin[19] working with high concentrations of gamboge particles found a deviation from the exponential law in the lower portion of the range which he investigated.

In conclusion, it seems that the work on colloidal suspensions leading to a uniform distribution was very likely not free from spurious effects and that there is no change in distribution law in increasing the height of a cell. Such a conclusion is certainly in harmony with the bulk of the other work related to this phase of the study of colloidal particles.

We wish to express our gratitude to the American Petroleum Institute for the funds furnished for this research, to Dr. R. A. Millikan for his interest as director of this project, to Mr. A. A. Grubb for his aid in the experimental work and to Dr. M. E. Nordberg for constructing the quartz cells.

[18] Burton, Alexander's "Colloid Chemistry," Vol. I, p. 165.

[19] Constantin, Comptes Rendus **158,** 1171 (1914).

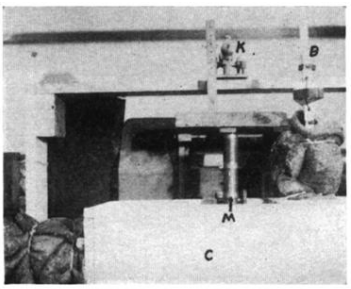

Fig. 2.

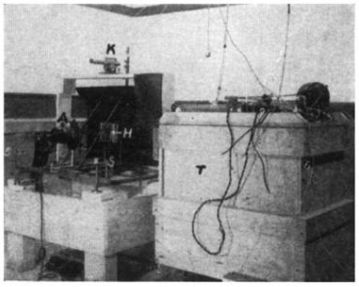

Fig. 3.